

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 825 166 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.02.1998 Bulletin 1998/09

(51) Int Cl.⁶: C07C 35/32, C11B 9/00

(21) Application number: 97306048.6

(22) Date of filing: 08.08.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE
Designated Extension States:
AL LT LV RO SI

(30) Priority: 22.08.1996 US 701665

(71) Applicant: INTERNATIONAL FLAVORS &
FRAGRANCES INC.
New York New York 10019 (US)

(72) Inventors:
• Narulan, Anubhav P.S.
County of Monmouth, New Jersey 07730 (US)

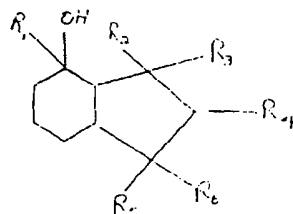
• Koestler, James Joseph
County of Monmouth, New Jersey 07730 (US)
• Hanna, Marie R.
County of Monmouth, New Jersey 07735 (US)
• Hattab, Honorine
New-York, County of NY State of New-York (US)
• Thibaudeau, Francis Charles Antoine
78600 Maisons Laffitte (FR)
• Beck, Charles E.J.
County of Union, New Jersey 07901 (US)

(74) Representative: Brown, John David et al
FORRESTER & BOEHMERT
Franz-Joseph-Strasse 38
80801 München (DE)

(54) Methyl substituted hexahydroindanol and perfumery uses thereof

(57) Described are methyl substituted hexahydroindanol-
danols defined according to the generic structure:

articles, cosmetic powders and hair preparations.



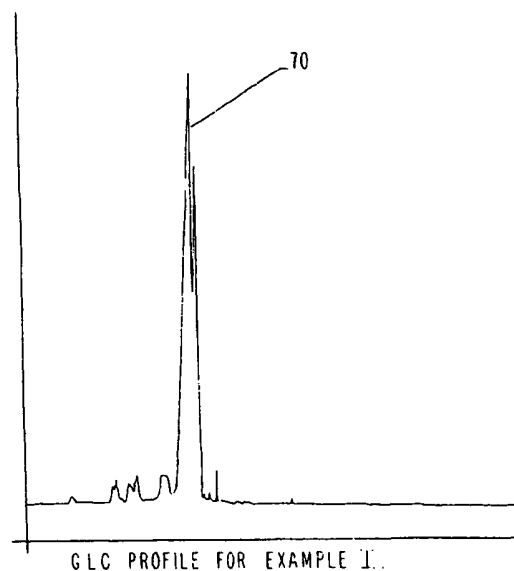
wherein R₁ is methyl and wherein R₂, R₃, R₅ and R₆
each represents methyl or ethyl with the provisos that:

(1) at least three of R₂, R₃, R₅ and R₆ represent me-
thyl; and

(2) when each of R₂, R₃, R₅ and R₆ is methyl, then
R₄ is methyl

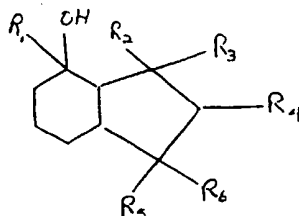
and uses thereof in augmenting or enhancing the aroma
of perfume compositions, colognes and perfumed arti-
cles including but not limited no perfumed polymers, sol-
id or liquid anionic, cationic, nonionic or zwitterionic de-
tergents, fabric softener compositions, fabric softener

FIG. 1



Description

The present invention provides methyl substituted hexahydroindanol defined according to the structure:

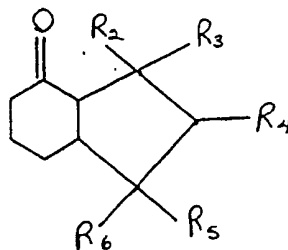


wherein R_1 is methyl and wherein R_2 , R_3 , R_5 and R_6 each represents methyl or ethyl with the provisos that:

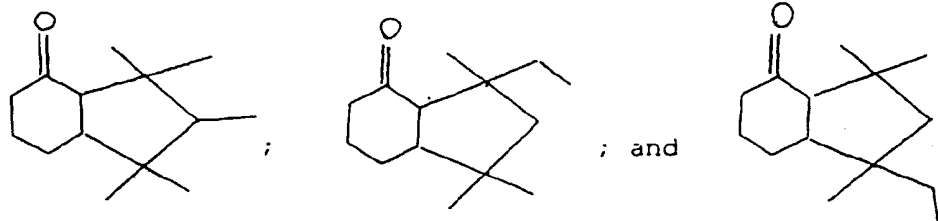
- (1) at least three of R_2 , R_3 , R_5 and R_6 represent methyl; and
- (2) when each of R_2 , R_3 , R_5 and R_6 is methyl, then R_4 is methyl.

The methyl substituted hexahydroindanol of our invention produced according to the processes of our invention are capable of augmenting, enhancing or imparting amber, fresh cut cedarwood, bois ambrene, limlewood (fir), cassis, juniper, animalic, musky and camphoraceous aromas with woody, amber, sandalwood, musky and kephalis topnotes in or to perfume compositions, colognes and perfumed articles (including soaps, anionic, cationic, nonionic or zwitterionic detergents, fabric softener articles, hair preparations and perfumed polymers).

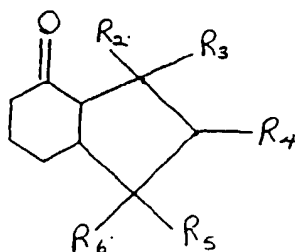
The methyl substituted hexahydroindanol of our invention are produced using as a starting material the mixture of ketones defined according to the structure:



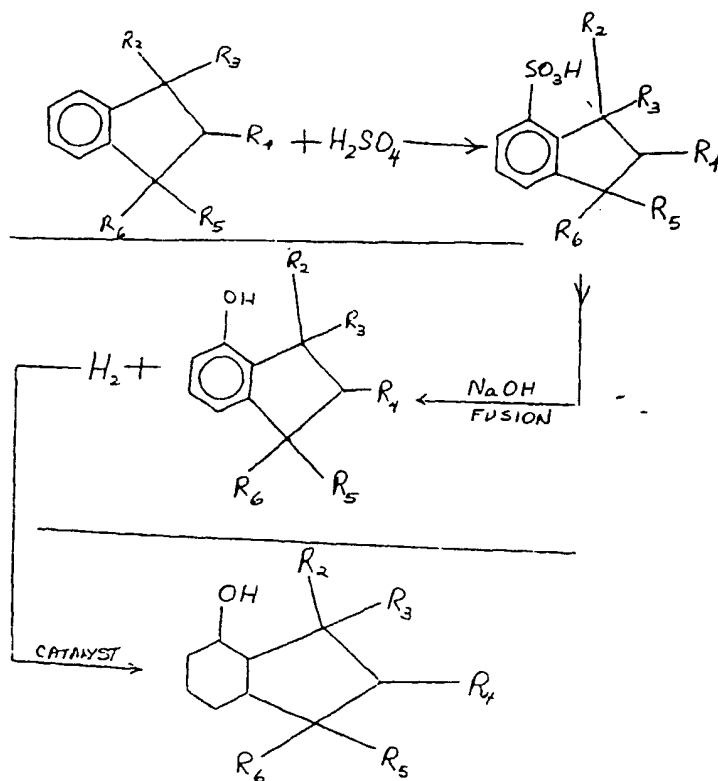
containing the compounds having the structures:



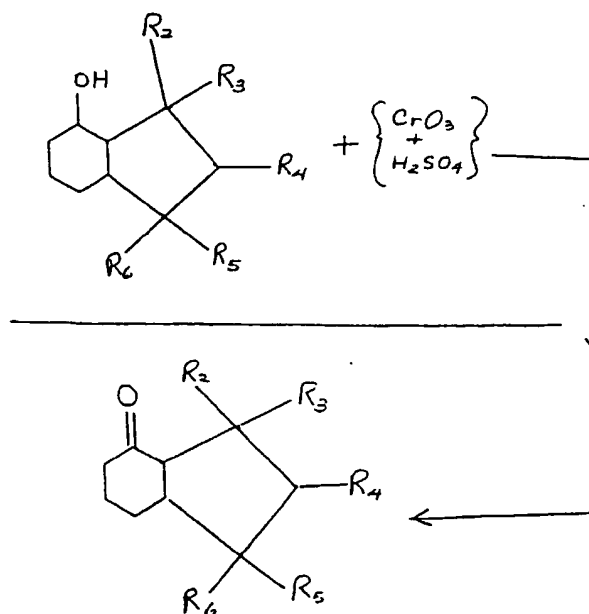
The mixture defined according to the structure:



wherein R_2 , R_3 , R_4 , R_5 and R_6 are defined, supra, is prepared according to the procedure set forth in Examples I and II at columns 5 and 6 of U.S. Letters Patent No. 3,681,464 issued on August 1, 1972 (title: "SATURATED INDANE DERIVATIVES AND PROCESSES FOR PRODUCING SAME") wherein the reaction sequence:

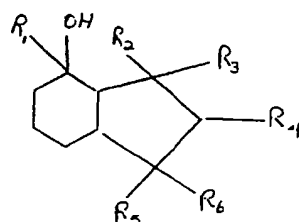


and

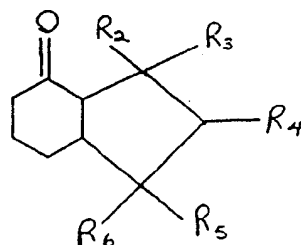


is set forth.

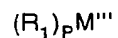
With reference to preparing the methyl substituted hexahydroindanols of our invention defined according to the structure:



the mixture of ketones defined according to the structure:

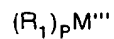


is reacted with an organometallic compound having the structure:



wherein R_1 is methyl; wherein P is the valence of M''' , which is 1 or 2; wherein M''' is a metal or a metal halide, M or M' ; wherein M represents Li or MgX ; wherein X is chloro, bromo or iodo; wherein M' is a bivalent metal, cadmium or zinc. Thus the compound having the structure:

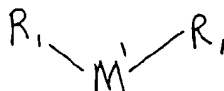
55



may either be a compound having the structure:

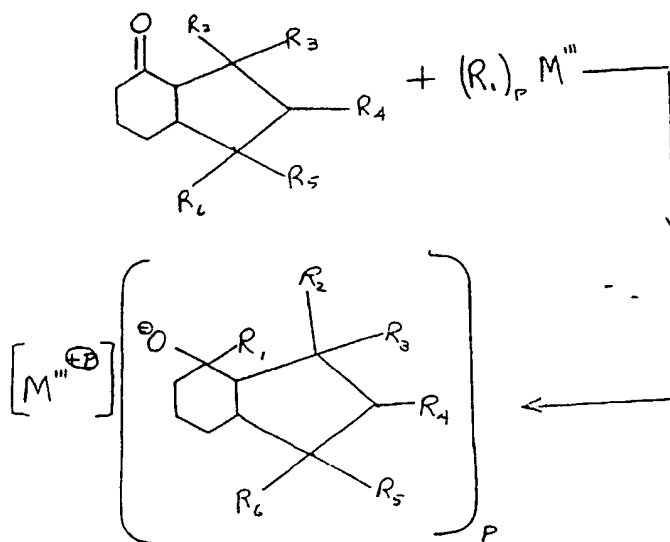


in the case of monovalent metals or metal halides, or the compound having the structure:

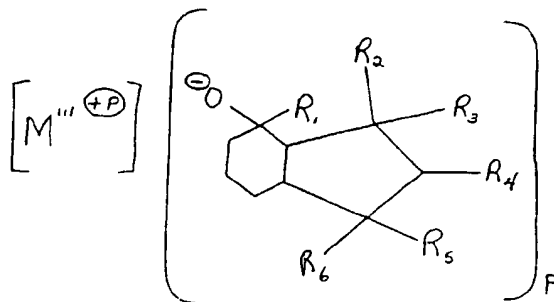


in the case of bivalent metals. The reaction takes place at low temperatures, e.g., -10°C up to $+10^\circ\text{C}$ in the presence of a solvent which is inert to the reactants, that is, diethyl ether (anhydrous) or tetrahydrofuran (anhydrous).

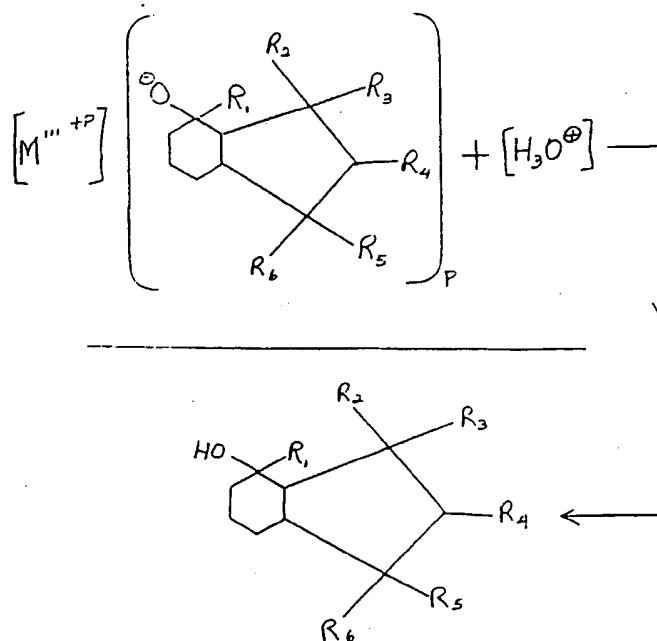
This reaction is set forth as follows:



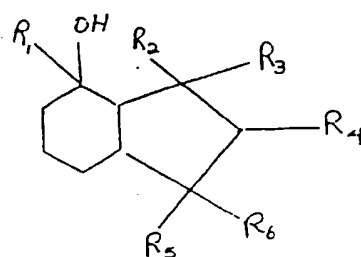
The resulting organometallic salt having the structure:



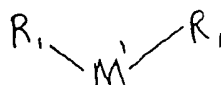
is then hydrolyzed in the presence of an acid, such as dilute hydrochloric acid or dilute ammonium chloride according to the reaction:



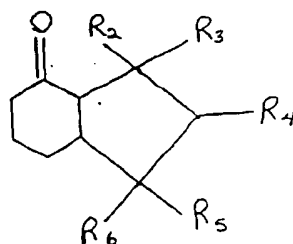
25 The resulting alcohol defined according to the structure:



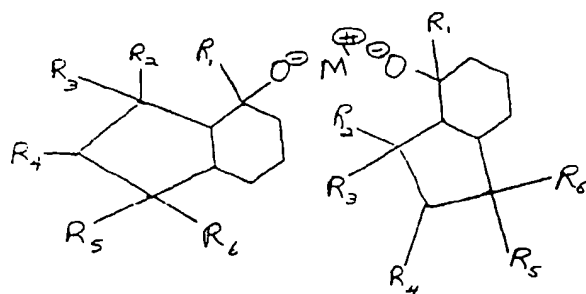
(wherein R₁ is methyl) is then fractionally distilled from the reaction mass and used for its perfumery properties.
With respect to the Grignard reaction, the organometallic salt formed when the reagent:



45 is reacted with a ketone or mixture of ketones defined according to the structure:



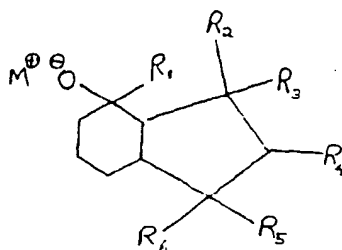
has the following structure:



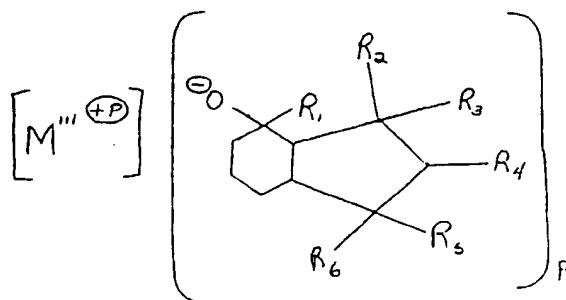
whereas when the Grignard reaction is carried out using the Grignard reagent having the structure:



the salt having the structure:



is formed. Both of the foregoing compounds are shown by the structure:

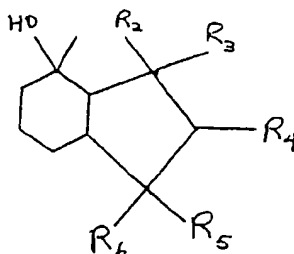


wherein M^+ , P , R_1 , R_2 , R_3 , R_4 , R_5 and R_6 have been defined, supra.

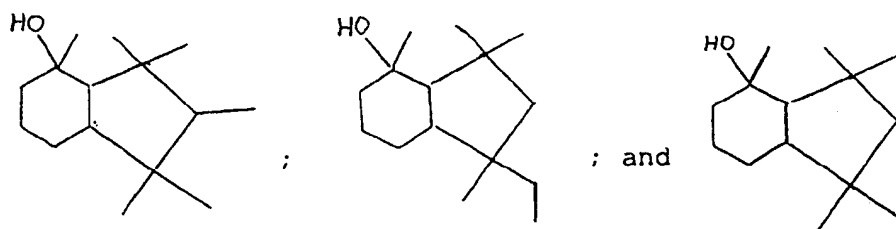
The Grignard reaction is carried out in the presence of an inert solvent such as tetrahydrofuran or diethyl ether as set forth, supra. The reaction temperature may vary between -10°C and $+10^\circ\text{C}$ for the formation of the salt, and the reaction temperature may vary between about 15°C up to about 30°C for the hydrolysis reaction. The mole ratio of ketone:Grignard reagent is preferably slightly greater than 1:1 in favor of the ketone (that is, where the ketone reactant is in excess). The concentration of Grignard reagent in solution (that is, in the inert solvent) may vary from about 0.5 up to about 1 mole per liter. In the hydrolysis reaction, other acidic medium may be used, for example, dilute acetic acid.

At the end of the reaction, the reaction mass is quenched with water and extracted with solvent, such as diethyl ether. The extract is stripped of solvent and distilled preferably by means of fractional distillation. The resulting fractions are bulked and utilized for their organoleptic properties.

The mixture of compounds having the structure:



containing the compounds having the structures:



(shown to be prepared according to Example I, bulked distillation fractions 15-23, *infra*), has an amber, cassis, juniper, bois ambrene, limlewood (fir), fresh cut cedarwood, animalic, musky and camphoraceous aroma with woody, sandalwood, amber, musky and kephalis topnotes.

The methyl substituted hexahydroindanols of our invention prepared in accordance with the processes of our invention are useful (taken alone or together with other ingredients in perfume compositions) as (an) olfactory component(s) in detergents and soaps, space odorants and deodorants, perfumes, colognes, toilet water, bath preparations such as creams, deodorants, hand lotions and sun screens; powders such as talcs, dusting powders, face powders, perfumed polymers and the like.

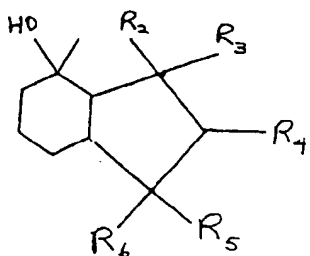
When used as an olfactory component, as little as 0.2% of the methyl substituted hexahydroindanols of our invention prepared in accordance with the process of our invention will suffice to impart an intense and long lasting, amber, fresh cut cedarwood, bois ambrene, limlewood (fir), cassis, juniper, animalic, musky and camphoraceous aroma with woody, amber, sandalwood, musky and kephalis topnotes to patchouli, vetiver and pine formulations. Generally, no more than 6% of the methyl substituted hexahydroindanols of our invention prepared in accordance with the process of our invention based on the ultimate end product are required in the perfumed article composition. Accordingly, the range of the use of the methyl substituted hexahydroindanols of our invention in a perfumed article may vary from about 0.2% up to about 6% by weight of the ultimate perfumed article.

Example I, *infra*, illustrates a method of our invention used to manufacture the methyl substituted hexahydroindanols of our invention. Examples II, *et seq.*, serve to illustrate the organoleptic utilities of the methyl substituted hexahydroindanols of our invention.

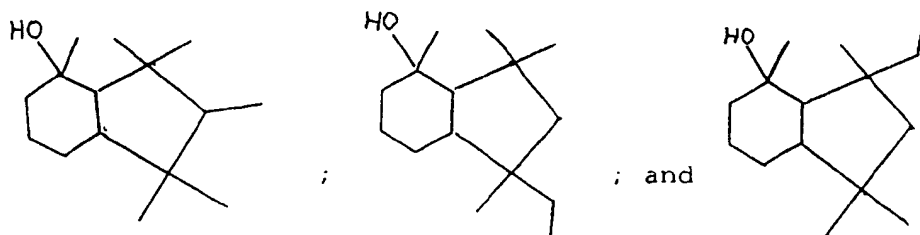
All parts and percentages given herein are by weight unless otherwise specified.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is the GLC profile for the reaction product of Example I containing the mixture of compounds defined according to the structure:

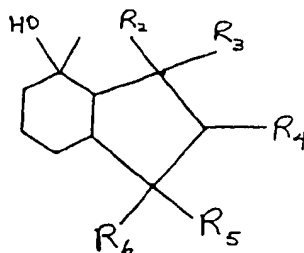


which includes the compounds having the structures:



(conditions: SE-30 column programmed from 150-220°C at 8°C per minute).

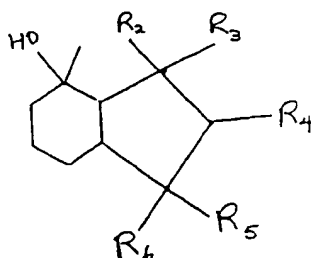
Figure 2 is the NMR spectrum for the mixture of compounds defined according to the structure:



prepared according to Example I.

Figure 2A is an enlargement of section "A" of the NMR spectrum of Figure 2.

Figure 3 is the infrared spectrum for the mixture of compounds defined according to the structure:



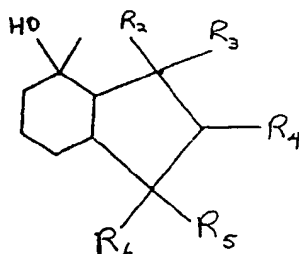
prepared according to Example I (wherein R₂, R₃, R₄, R₅ and R₆ are defined, supra).

Figure 4 represents a cutaway side elevation view of apparatus used in forming perfumed polymers which contain embedded therein at least one of the methyl substituted hexahydroindanols of our invention.

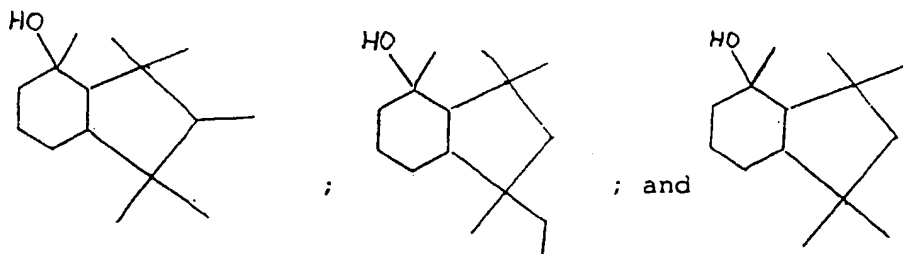
Figure 5 is a front view of the apparatus of Figure 4 looking in the direction of the arrows along lines 5-5.

DETAILED DESCRIPTION OF THE DRAWINGS

Figure 1 is the GLC profile for the reaction product of Example 1. The peak indicated by reference numeral 70 is the peak for the mixture of compounds having the structure:



which is a mixture of the compounds having the structures:



Referring to Figures 4 and 5, there is provided a process for forming scented polymer elements (wherein the polymer may be a thermoplastic polymer such as low density polyethylene or polypropylene or copolymers of ethylene and vinyl acetate or mixtures of polymers and copolymers such as copolymers of ethylene and vinyl acetate and polyethylene) such as pellets useful in the formation of plastic particles useful in fabricating certain articles which may be perfumed. This process comprises heating the polymer or mixture of polymers to the melting point of said polymer or mixture of polymers, e.g., 250°C in the case of low density polyethylene. The lower most portion of the container is maintained at a slightly lower temperature and the material in the container is taken off at such location for delivery through the conduit (indicated by reference numeral 218). Thus, referring to Figures 4 and 5, in particular, the apparatus used in producing such elements comprises a device for forming the polymer containing perfume, e.g., polyethylene or polyethylene-polyvinyl acetate or mixtures of same or polypropylene, which comprises a vat or container 212 into which the polymer taken alone or in admixture with other copolymers and the perfuming substance which is the methyl substituted hexahydroindanol mixture of our invention and other compatible perfumes is placed. The container is closed by means of an air-tight lid 228 and clamped to the container by bolts 265. A stirrer 273 traverses the lid or cover 228 in an air-tight manner and is rotatable in a suitable manner. A surrounding cylinder 212A having heating coils which are supplied with electric current through cable 214 from a rheostat or control 216 is operated to maintain the temperature inside the container 212 such that the polymer in the container will be maintained in the molten or liquid state. It has been found advantageous to employ polymers at such a temperature that the viscosity will be in the range of 90-100 Saybolt seconds. The heater is operated to maintain the upper portion of the container 212 within a temperature range of, for example, 220-270°C in the case of low density polyethylene. The bottom portion of the container 212 is heated by means of heating coils 212A regulated through the control 220 connected thereto through a connecting wire 222 to maintain the lower portion of the container 212 within a temperature range of 220-270°C.

Thus, the polymer or mixture of polymers added to the container 212 is heated from 10-12 hours, whereafter the perfume composition or perfume material which contains the methyl substituted hexahydroindanol mixture of our invention is quickly added to the melt. Generally, about 10-45% by weight of the resulting mixture of the perfumery substance is added to the polymer.

After the perfume material is added to the container 212, the mixture is stirred for a few minutes, for example, 5-15 minutes and maintained within the temperature ranges indicated previously by the heating coils 212A. The controls 216 and 220 are connected through cables 224 and 226 to a suitable supply of electric current for supplying the power for heating purposes.

Thereafter, the valve "V" is opened permitting the mass to flow outwardly through conduit 232 (also shown by reference numeral 218 (in cutaway cross section)) having a multiplicity of orifices 234 adjacent to the lower side thereof.

The outer end of the conduit 232 is closed so that the liquid polymer in intimate admixture with the methyl substituted hexahydroindanol mixture of our invention and one or more other substances (if desired) will continuously drop through the orifices 234 downwardly from the conduit 232. During this time, the temperature of the polymer intimately admixed with the perfumery substance in the container 212 is accurately controlled so that a temperature in the range of from about 240-250°C, for example in the case of low density polyethylene), will exist in the conduit 232. The regulation of the temperature through the controls 216 and 220 is essential in order to ensure temperature balance to provide for the continuous dripping or dropping of molten polymer intimately admixed with the perfume substance which contains the methyl substituted hexahydroindanol mixture of our invention, through the orifices 234 at a rate which will ensure the formation of droplets 236 which will fall downwardly onto a moving conveyor belt 238 caused to run between conveyor wheels 240 and 242 beneath the conduit 232.

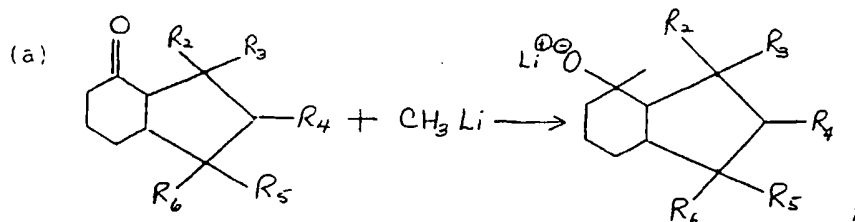
When the droplets 236 fall onto the conveyor 238, they form pellets 244 which harden almost instantaneously and fall off the end of the conveyor 238 into a container 245 which is advantageously filled with water 252 or some other suitable cooling liquid to ensure the rapid cooling of each of the pellets 244. The pellets 244 are then collected from the container 245 and utilized for the formation of other functional products, e.g., garbage bags and the like.

A feature of the invention is the provision for the moistening of the conveyor belt 238 to ensure the rapid formation of the solid polymer-aromatizing agent containing pellets 244 without sticking to the belt. The belt 238 is advantageously of a material which will not normally stick to a melted polymer, but the moistening means 248 ensures a sufficiently cold temperature of the belt surface for the adequate formation of the pellets 244. The moistening means comprises a container 250 which is continuously fed with water 252 to maintain a level 254 for moistening a sponge element 256 which bears against the exterior surface of the belt 238.

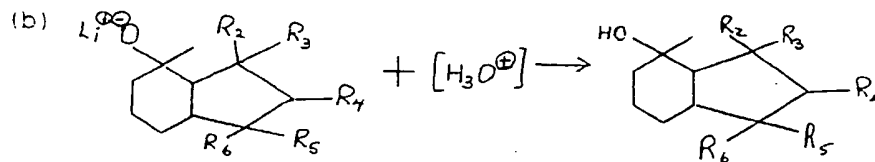
EXAMPLE I

PREPARATION OF 4-METHYL-HEXAHYDRO-METHYL SUBSTITUTED-4-INDANOL

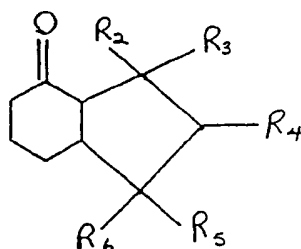
Reactions:



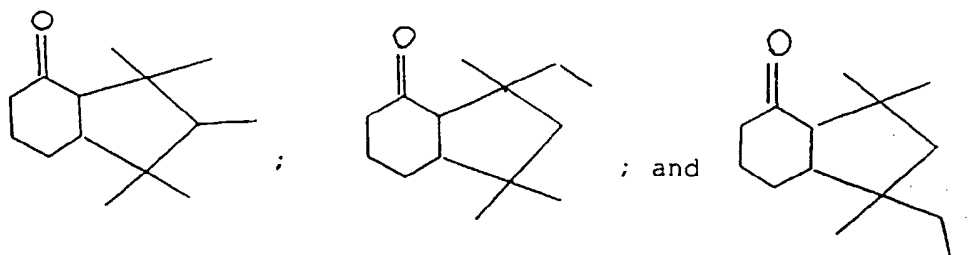
and



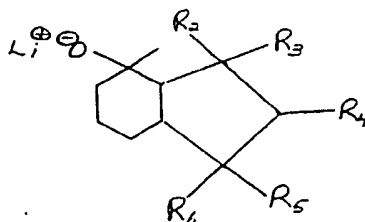
Into a 5 liter reaction vessel equipped with stirrer, thermometer, reflux condenser, heating mantle and cooling coils is placed a solution containing 2.24 moles methyl lithium in 600 ml of tetrahydrofuran. The contents of the reaction vessel is cooled to 0°C. Over a period of 1 hour, 333 grams (1.6 moles) of the mixture of ketones defined according to the structure:



(a mixture of compounds having the structures:



is added to the reaction mass while maintaining the reaction temperature at between -2°C and 0°C. The reaction mass is then maintained at 0°C with stirring for a period of 3 hours. At this point in time, the reaction mass contains a solution of the organometallic salt having the structure:



wherein in the mixture in each of the compounds R₂, R₃, R₄, R₅ and R₆ are as defined, supra

The reaction mass is quenched with 1 liter of 4 molar aqueous hydrochloric acid. The reaction mass now exists in two phases: an organic phase and an aqueous phase. The organic phase is separated from the aqueous phase.

The organic phase is washed as follows:

(a) four 1 liter portions of saturated aqueous sodium bicarbonate;

(b) one 1 liter portion of water; and

(c) one 1 liter portion of saturated aqueous sodium chloride.

The resulting product is then filtered through CELITE®/anhydrous sodium sulfate. The resulting product is then fractionally distilled yielding the following fractions:

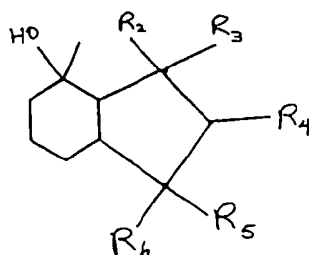
Fraction Number	Vapor Temperature (°C)	Liquid Temperature (°C)	Vacuum mm/Hg Pressure
1	33/72	75/120	42/1.66
2	90	114	1.45
3	84	150	1.58

Fractions 2 and 3 are bulked and redistilled yielding 30 fractions. Fractions 15-23 distilling at 88-91°C (vapor

temperature) and a vacuum of 1.44-1.6 mm/Hg are bulked.

The bulked fractions consist of a mixture of compounds defined according to the structure:

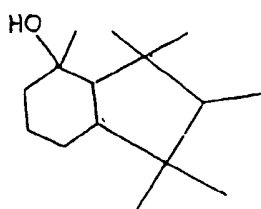
5



10

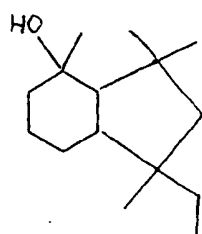
(the compounds having the structures:

15

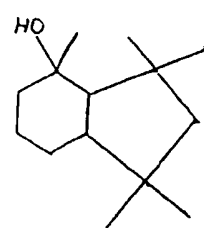


20

;



; and



)

25

(wherein R₂, R₃, R₄, R₅ and R₆ are defined, supra) as confirmed by NMR, IR and mass spectral analyses.

EXAMPLE II

30

The following Chypre formulation is prepared:

35

40

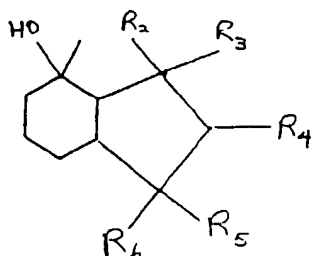
45

50

55

Ingredients	Parts by Weight
Musk ambrette	40
Musk ketone	60
Coumarin	30
Oil of bergamot	150
Oil of lemon	100
Methyl ionone	50
Hexyl cinnamic aldehyde	100
Hydroxycitronellal	100
Oil of lavender	50
Texas cedarwood oil	85
Virginia cedarwood oil	30
Oil of sandalwood (East Indies)	40
Isoeugenol	20
Eugenol	10
Benzyl acetate	30
β -phenyl ethyl alcohol	40
α -phenyl ethyl alcohol	30
Oakmoss absolute	30
Vetiver oil of Venezuela	25
<p data-bbox="345 1182 876 1239">The mixture of compounds defined according to the structure:</p> <div data-bbox="597 1255 799 1432"> </div> <p data-bbox="345 1444 912 1501">(a mixture of compounds having the structures:</p> <div data-bbox="376 1528 1019 1675"> </div> <p data-bbox="345 1749 990 1806">prepared according to Example I, bulked distillation fractions 15-23.</p>	25

The mixture of compounds defined according to the structure:



imparts to this Chypre formulation amber, cassis, juniper, bois ambrene, limlewood (fir), fresh cut cedarwood, animalic, musky and camphoraceous undertones with woody, sandalwood, amber, musky and kephalis topnotes. Accordingly, the perfume formulation of this Example II is described as:

"a Chypre aroma with amber, cassis, juniper, bois ambrene, limlewood (fir), fresh cut cedarwood, animalic, musky and camphoraceous undertones with woody, sandalwood, amber, musky and kephalis topnotes".

EXAMPLE III

PREPARATION OF COSMETIC POWDER COMPOSITIONS

Cosmetic powder compositions are prepared by mixing in a ball mill 100 grams of talcum powder with 0.25 grams of each of the substances set forth in Table I below. Each of the cosmetic powder compositions has an excellent aroma as described in Table I below.

TABLE I

Substance	Aroma Description
<p>The mixture of compounds defined according to the structure:</p> <p>prepared according to Example I, bulked distillation fractions 15-23.</p>	<p>An amber, cassis, juniper, bois ambrene, limlewood (fir), fresh cut cedarwood, animalic, musky and camphoraceous aroma with woody, sandalwood, amber, musky and kephalis topnotes.</p>
<p>The perfume composition of Example II.</p>	<p>A Chypre aroma with amber, cassis, juniper, bois ambrene, limlewood (fir), fresh cut cedarwood, animalic, musky and camphoraceous undertones with woody, sandalwood, amber, musky and kephalis topnotes.</p>

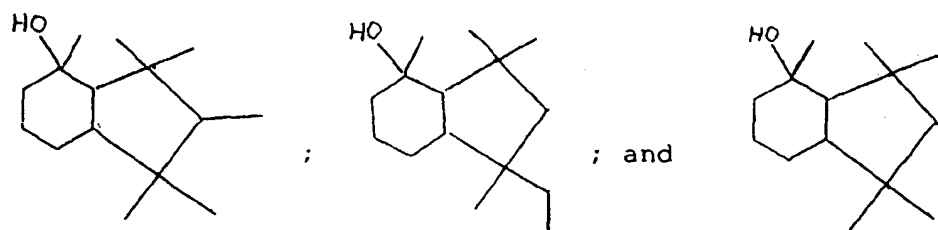
EXAMPLE IV**PERFUMED LIQUID DETERGENTS**

Concentrated liquid detergents (lysine salt of n-dodecylbenzene sulfonic acid as more specifically described in U. S. Patent No. 3,948,818 issued April 6, 1976, incorporated by reference herein) with aroma nuances as set forth in Table I of Example II are prepared containing 0.10%, 0.15%, 0.20%, 0.25%, 0.30% and 0.35% of the substance set forth in Table I of Example II. They are prepared by adding and homogeneously mixing the appropriate quantity of substance set forth in Table I of Example II in the liquid detergent. The detergents all possess excellent aromas as set forth in Table I of Example II, the intensity increasing with greater concentrations of substance as set forth in Table I of Example II.

The features disclosed in the foregoing description, in the following claims/and or in the accompanying drawings may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

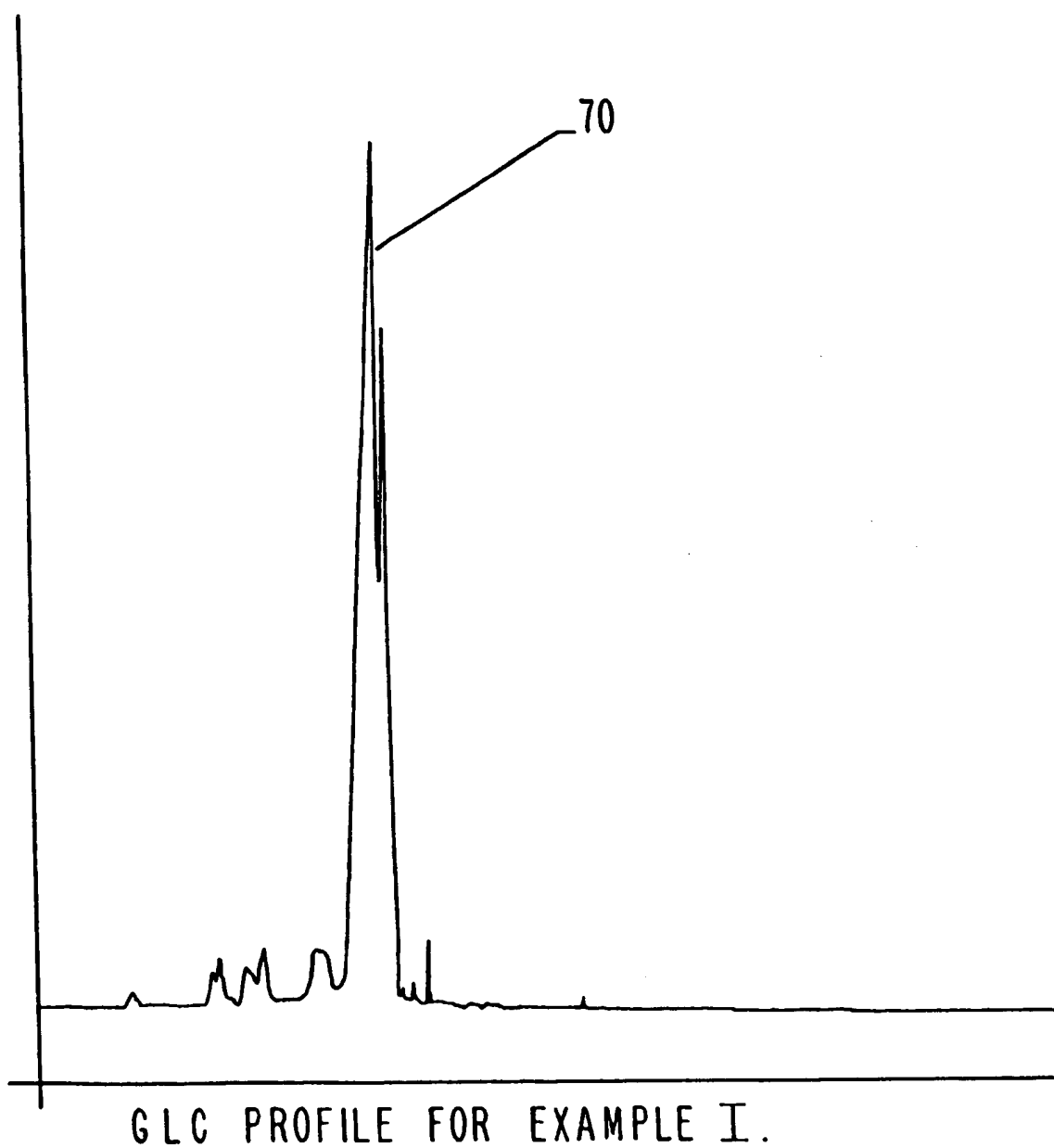
Claims

1. A composition comprising a mixture consisting of the compounds having the structures:



2. A process for augmenting or enhancing the aroma of a perfume composition, cologne or perfumed article comprising the step of intimately admixing with a perfume base, a cologne base or a perfumed article base an aroma imparting, augmenting or enhancing quantity and concentration of the composition of matter defined according to Claim 1.
3. A perfume composition comprising a perfume base and intimately admixed therewith an aroma augmenting, enhancing or imparting quantity and concentration of the composition of matter of Claim 1.
4. A perfumed article comprising a perfumed article base and intimately admixed therewith an aroma augmenting, enhancing or imparting quantity and concentration of the composition of matter defined according to Claim 1.
5. A cologne consisting of water, ethanol and an aroma imparting quantity of the methyl substituted hexahydroindanol mixture defined according to Claim 1.
6. A perfumed polymer comprising a microporous polymer and intimately admixed therewith in the interstices thereof the composition of matter defined according to Claim 1.
7. A perfumed polymer comprising a microporous polymer and intimately admixed in the interstices thereof the perfume composition of Claim 3.

FIG. 1



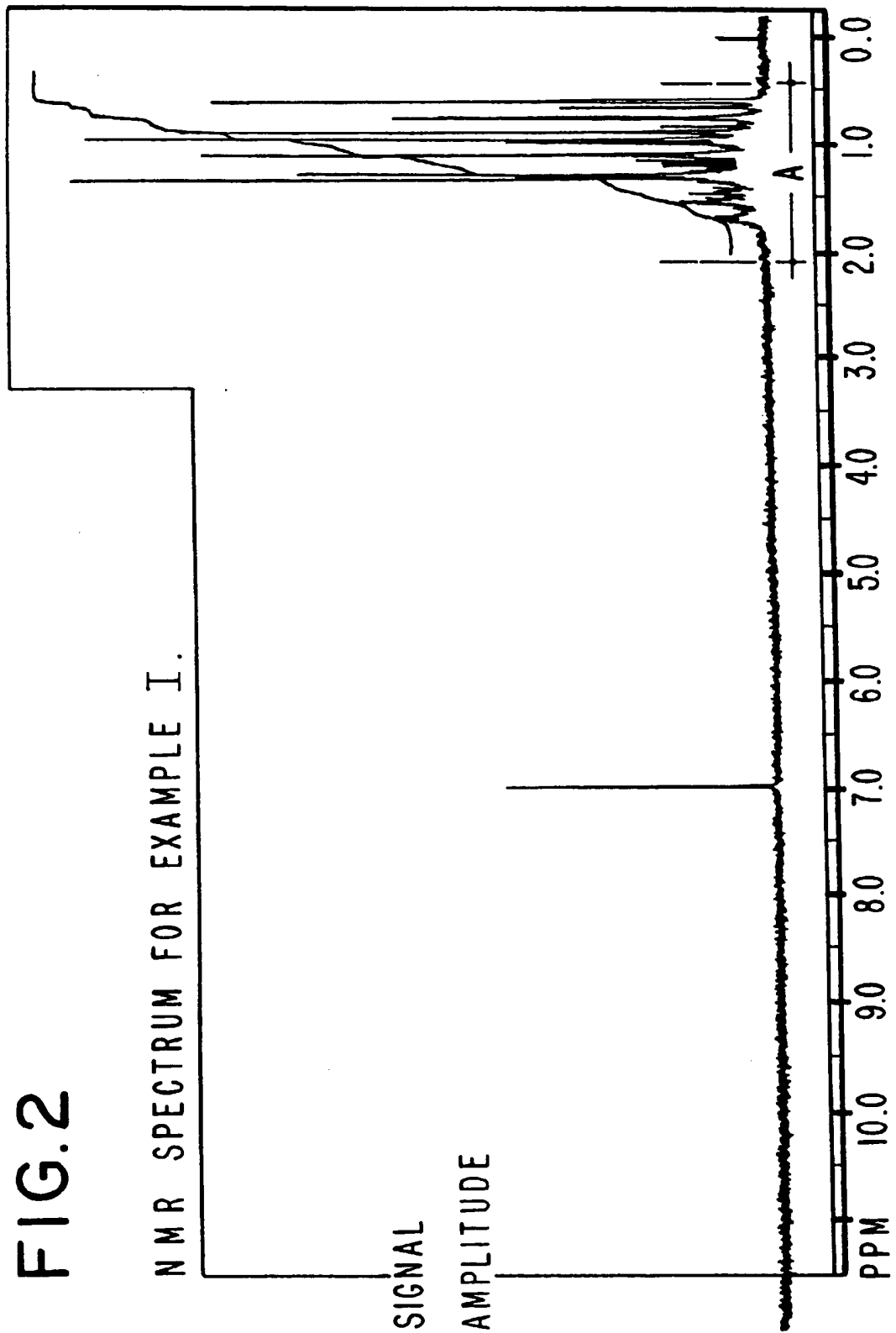
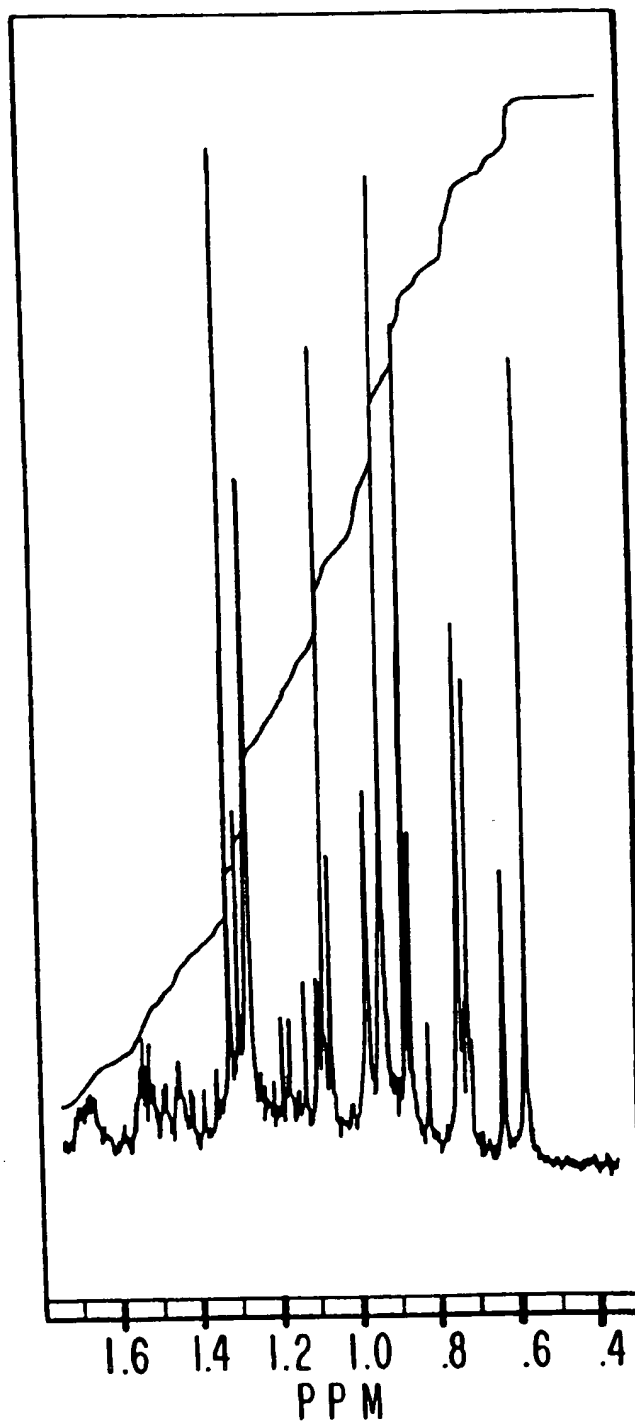


FIG. 2A



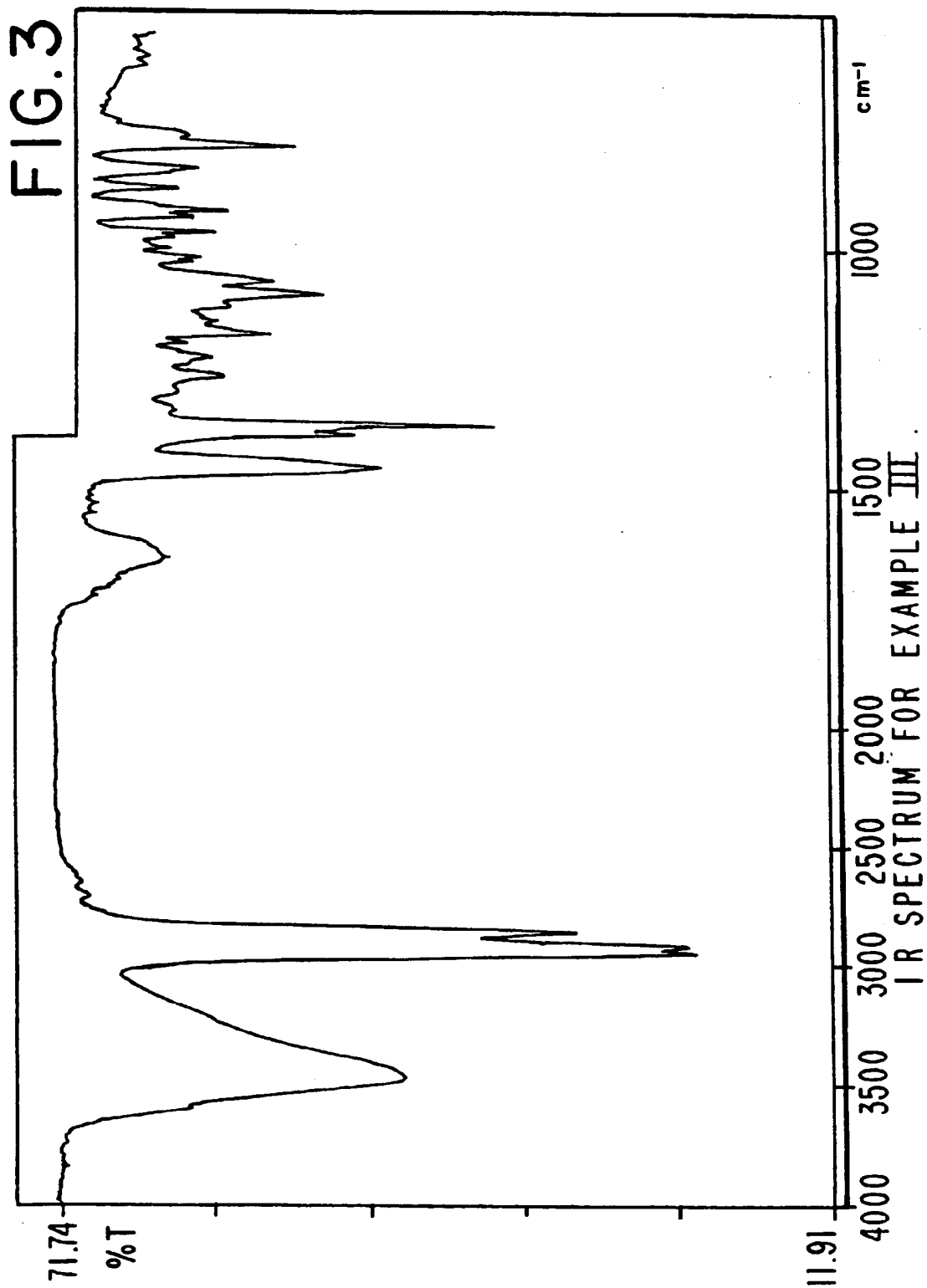


FIG. 4

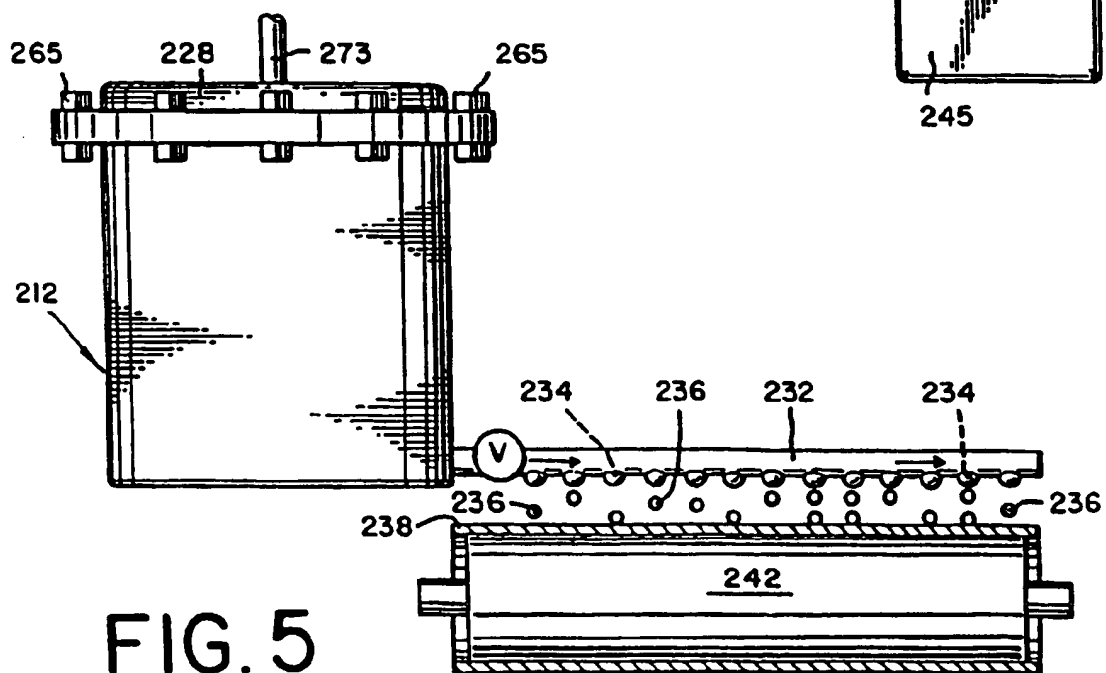
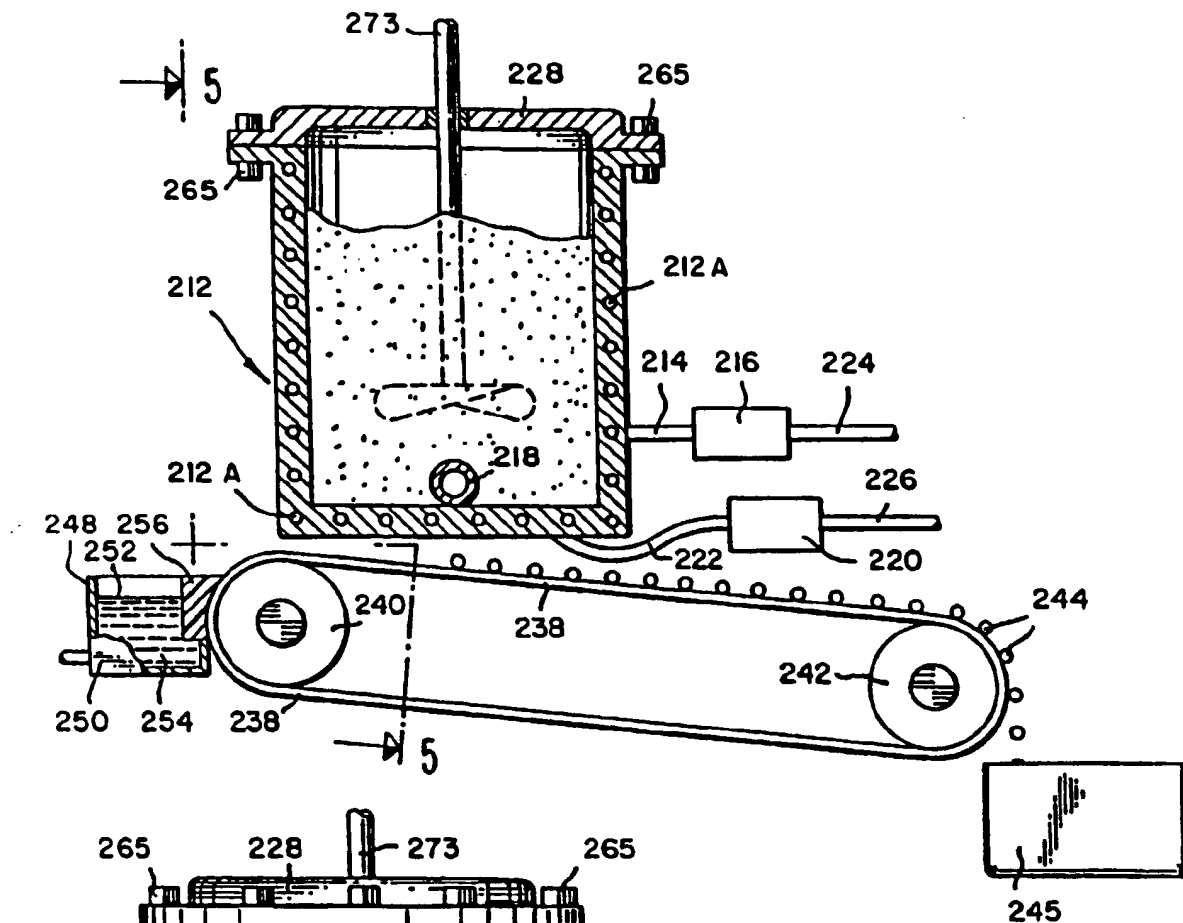
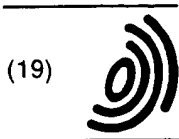


FIG. 5



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 825 166 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
14.04.1999 Bulletin 1999/15

(51) Int Cl.⁶: C07C 35/32, C11B 9/00

(43) Date of publication A2:
25.02.1998 Bulletin 1998/09

(21) Application number: 97306048.6

(22) Date of filing: 08.08.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE
Designated Extension States:
AL LT LV RO SI

- Koestler, James Joseph
County of Monmouth, New Jersey 07730 (US)
- Hanna, Marie R.
County of Monmouth, New Jersey 07735 (US)
- Hattab, Honorine
New-York, County of NY State of New-York (US)
- Thibaudeau, Francis Charles Antoine
78600 Maisons Laffitte (FR)
- Beck, Charles E.J.
County of Union, New Jersey 07901 (US)

(30) Priority: 22.08.1996 US 701665

(71) Applicant: INTERNATIONAL FLAVORS &
FRAGRANCES INC.
New York New York 10019 (US)

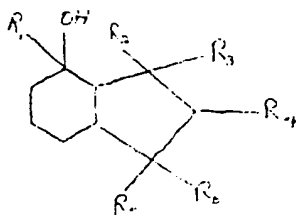
(74) Representative: Brown, John David et al
FORRESTER & BOHMERT
Franz-Joseph-Strasse 38
80801 München (DE)

(72) Inventors:
• Narulan, Anubhav P.S.
County of Monmouth, New Jersey 07730 (US)

(54) Methyl substituted hexahydroindanol and perfumery uses thereof

(57) Described are methyl substituted hexahydroindanol defined according to the generic structure:

tergents, fabric softener compositions, fabric softener articles, cosmetic powders and hair preparations.



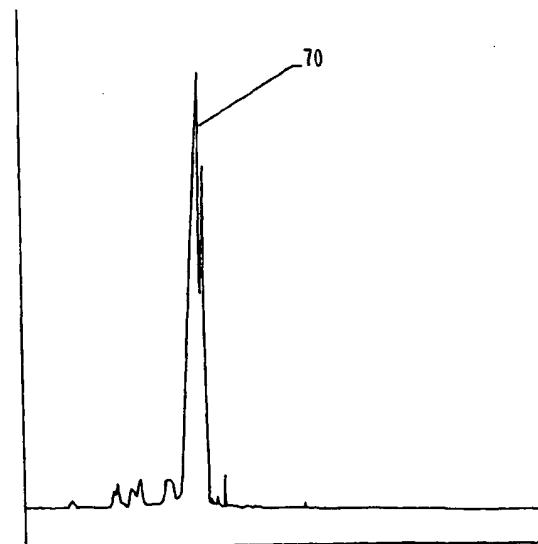
wherein R₁ is methyl and wherein R₂, R₃, R₅ and R₆ each represents methyl or ethyl with the provisos that:

(1) at least three of R₂, R₃, R₅ and R₆ represent methyl; and

(2) when each of R₂, R₃, R₅ and R₆ is methyl, then R₄ is methyl

and uses thereof in augmenting or enhancing the aroma of perfume compositions, colognes and perfumed articles including but not limited no perfumed polymers, solid or liquid anionic, cationic, nonionic or zwitterionic de-

FIG. I



GLC PROFILE FOR EXAMPLE I.

P 0 825 166 A3

EP 0 825 166 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 6048

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 3 767 713 A (E. THEIMER) 23 October 1973 * column 1 - column 2; claims; examples I,III *	1,2	C07C35/32 C11B9/00
A	US 4 576 740 A (J.B. HALL, ET AL.) 18 March 1986 * column 6; claims; examples I-III *	1,2	
A	US 4 514 324 A (W.J. EVERS, ET AL.) 30 April 1985 * column 12; claim; examples III,XVI *	1,2	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07C C11B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 February 1999	Examiner English, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EP 0 825 166 A3 (1999/02/18)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 97 30 6048

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-02-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3767713 A	23-10-1973	US 3806472 A	23-04-1974
		US 3636165 A	18-01-1972
		US 3636176 A	18-01-1972
		US 3647826 A	07-03-1972
		US 3681464 A	01-08-1972
		US 3773836 A	20-11-1973
		BE 753751 A	22-01-1971
		CA 992549 A	06-07-1976
		CH 523962 A	15-06-1972
		DE 2036936 A	08-07-1971
		DE 2064918 A	23-09-1971
		DE 2064919 A	16-09-1971
		DE 2064920 A	30-09-1971
		DE 2064921 A	16-09-1971
		FR 2058364 A	28-05-1971
		GB 1300970 A	29-12-1972
		NL 7012137 A,B	22-02-1971
		NL 7600397 A,B,	29-04-1976
		NL 7600398 A,B,	29-04-1976
		NL 7600399 A,B,	29-04-1976
		NL 7600400 A,B,	29-04-1976
		NL 7600401 A,B,	29-04-1976
US 4576740 A	18-03-1986	US 4520032 A	28-05-1985
		EP 0154918 A	18-09-1985
		JP 1397914 C	07-09-1987
		JP 60208934 A	21-10-1985
		JP 62005894 B	07-02-1987
		US 4535192 A	13-08-1985
		US 4576186 A	18-03-1986
US 4514324 A	30-04-1985	US 4548821 A	22-10-1985
		US 4434085 A	28-02-1984
		US 4471135 A	11-09-1984
		US 4512902 A	23-04-1985
		US 4532359 A	30-07-1985
		US 4496775 A	29-01-1985
		US 4549972 A	29-10-1985

